



High pressure phase behavior of carbon dioxide in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium dicyanamide ionic liquids

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ABSTRACT

The acidity/basicity of the reaction media has a substantial influence on the efficiency of many reactive processes; therefore, a new class of acidic or basic ionic liquids is gaining special attention due to the possibility of increasing the efficiency of many processes by a wise manipulation of their properties. The absorption of sour gases is one of the processes that can be enhanced by the basic character of the ionic liquid. The fluorination of the cation or anion can also contribute to the gas solubility enhancement. In this work, these two characteristics are evaluated and compared through the study of gas–liquid equilibrium of two ionic liquids, 1-butyl-3-methylimidazolium dicyanamide ([C₄mim][DCA]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][Tf₂N]), with carbon dioxide (CO₂) at temperatures up to 363 K and pressures up to 74 MPa.

A thermodynamic model based on the Peng–Robinson equation of state with the Wong–Sandler mixing rule, using the UNIQUAC model for the activity coefficients, was used to describe the experimental data and for the estimation of the Henry's constants.

The solubility of CO₂ in 1-butyl-3-methylimidazolium dicyanamide is much lower than anticipated on the basis of the reported pK_a of the anion when compared with the acetate anion. No chemisorption is observed and the solvation enthalpy is quite low, ruling out any Lewis acid/base interaction between the anion and the CO₂. The 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, known to present one of the highest solubilities towards CO₂ due to the presence of fluoroalkyl groups, showed a much larger solubility for CO₂ than 1-butyl-3-methylimidazolium dicyanamide.

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1. Introduction

Acidic or basic ionic liquids (ILs) represent new classes of acids or bases. The study of the acidity/basicity of these task-specific ionic liquids is of great importance since the efficiency of many processes depends on the acidity/basicity of the media or can be controlled by it. These compounds aptness for the fine tuning of their properties through an endless combination of cations and anions, cataloging them as *designer* solvents, allow the design of solvents for the development of more efficient and sustainable processes and products. From the wide range of applications envisioned for ILs, such as catalysts for acid-catalyzed organic reactions [1,2], hydrosilation processes [3], lubricants [4], performance additives [5], media for metal-catalyzed reactions [6], their use as CO₂-selective separation media [7–10] for capture/sequestration

of sour gases like CO₂, H₂S and SO₂ is one of the most exciting and of increasing interest [8,9,11–27]. The development of improved, highly efficient and economically viable separation and storage processes is gaining a special interest both by academia and industry. Nonetheless, and despite of the promising properties of ILs, further research is still required in order to make this *neoteric* solvents feasible candidates for these applications. Being a key parameter in the design of equilibrium stage- and rate-based separations, reliable gas solubility data is of great interest and a fundamental step towards the development of industrial applications, either by the data itself or by developing predictive and simulation tools to aid in such applications development.

Crowhurst et al. [28] reported that the hydrogen bond basicities of ILs are controlled by the anion, while the hydrogen bond donation behavior is dominated by the hydrogen bond basicity of the anions with a smaller contribution from the hydrogen bond acidity of the cation. Therefore, changing to more basic anions leads to a dramatic drop in the acidity. Based on the Pearson's "hard and

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soft acid/base” principles, allowing a strong affinity towards CO₂, Pennline et al. [29] screened quaternary ammonium polyether ILs as potential solvents for CO₂ capture. In a previous work [12], following the works by Shiflett et al. [26] and Yokozeki et al. [30], imidazolium-based IL with the acetate and trifluoroacetate anions were studied by our group. The acetate ion was shown to present a chemical absorption behavior for low CO₂ mole fractions (mole fractions < 0.3) and *ab initio* calculations and ¹³C HRMAS NMR spectroscopy provided a deeper understanding of the CO₂–acetate interactions [12].

In the wake of this previous work [12], the purpose of the present study is to further explore the basicity of the anion as a mean to enhance the absorption of carbon dioxide by the ionic liquids. For that purpose, following the suggestion of MacFarlane et al. [31] that dicyanamide would be a basic anion (the pK_a, 5.1, for dicyanoamine reported by MacFarlane is higher than the pK_a for the acetic acid, 4.75), a dicyanamide anion based ionic liquid was chosen here to further investigate the effect of the anion basicity on the solvation of CO₂. The 1-butyl-3-methylimidazolium dicyanamide was thus selected for that purpose and the solubility of the CO₂ in this IL is compared to that in the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, also studied here and known to present one of the highest solubility towards CO₂ due to the presence of fluoroalkyl groups. Both systems were measured at temperatures up to 363 K and pressures up to 74 MPa.

The Peng–Robinson equation of state [32] with the Wong–Sandler/UNIQUAC mixing rule [33] using the UNIQUAC model [34] for the activity coefficients, was used to model the experimental data measured in this work.

2. Experimental

2.1. Materials

Two ILs based on the 1-butyl-3-methyl-imidazolium cation, 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [C₄mim][Tf₂N] and 1-butyl-3-methyl-imidazolium dicyanamide, [C₄mim][DCA], were used in this study. All compounds were acquired at IoLiTec with mass fraction purities higher than 99% and bromide impurity mass fraction lower than 10^{−4}. The purities stated by the supplier, of each ionic liquid, were checked by ¹H NMR, ¹³C NMR and ¹⁹F NMR.

It is well known that the phase equilibria and thermophysical properties of ILs are greatly influenced by their water content [35–38]. Blanchard et al. [16] reported that minor amounts of water, dissolved in [C₄mim][PF₆], lead to a reduction of 77% on the CO₂ solubility. Later, in a systematically study on the influence of water on the solubility of CO₂ for the same compound, Fu et al. [39] reported a less pronounced though significant influence, <15%. Furthermore, being an active proton acceptor, water can dramatically increase the degree of dissociation of an acid in a neutral ionic liquid. Similarly, in a neutral IL the state of a base will be altered by the presence of water and in a basic IL, water will be at least partly dissociated producing OH[−] [31]. These reports made researchers aware of the importance of implementing purifying procedures prior to the measurements. Thus, in order to reduce to negligible values both water and volatile compounds, vacuum (0.1 Pa), stirring and moderate temperature (353 K), for a period of at least 48 h, were applied prior to the measurements. The final IL water content was determined with a Metrohm 831 Karl Fischer coulometer, indicating a water mass fraction of (44 and 28) × 10^{−6} for [C₄mim][Tf₂N] and [C₄mim][DCA], respectively.

The carbon dioxide (CO₂) was acquired from Air Liquide with a purity of ≥99.998% and H₂O, O₂, C_nH_m, N₂ and H₂ impurities volume fractions lower than (3, 2, 2, 8 and 0.5) × 10^{−6}, respectively.

2.2. Experimental equipment

The high pressure equilibrium cell used in this work is based on a cell designed by Daridon and co-workers [40–44] using the synthetic method. Both the apparatus and the methodology followed here were fully described in previous works [11,12], and shown to be adequate to accurately measure vapor–liquid phase equilibrium in a wide range of pressures and temperatures [11,12,40–44]. The high pressure equilibrium cell consists of a horizontal hollow stainless-steel cylinder, closed at one end by a movable piston and at the other end by a sapphire window. This window, along with a second window on the cell wall through which an optical fiber lights the cell chamber, allows the operator to follow the behavior of the sample with pressure and temperature. The orthogonal positioning of both sapphire windows minimizes the parasitic reflections and improves the observation in comparison to axial lighting. A small magnetic bar placed inside the cell allows the homogenization of the mixture by means of an external magnetic stirrer. The presence of the magnetic stirrer, as well as the cell reduced volume, help to minimize the inertia and temperature gradients within the sample. The cell is thermostated by circulating a heat-carrier fluid through three flow lines directly managed into the cell. The heat-carrier fluid is thermo-regulated with a temperature stability of ±0.01 K by means of a thermostat bath circulator (Julabo MC). The temperature is measured with a high precision thermometer, Model PN 5207 with an accuracy of 0.01 K, connected to a calibrated platinum resistance inserted inside the cell close to the sample. The pressure is measured by a piezoresistive silicon pressure transducer (Kulite) fixed directly inside the cell to reduce dead volumes, that was previously calibrated and certified by an independent laboratory with IPAC accreditation, following the EN 837-1 standard and with accuracy better than 0.2%.

A fixed amount of IL was introduced inside the cell, its exact mass was determined by weighting, using a high weight/high precision balance with an accuracy of 1 mg (Sartorius). In order to avoid any interference of atmospheric gases during the manipulation, after placing the IL inside the cell, it was kept under vacuum overnight, while stirring and heating at 353 K.

The CO₂ was introduced under pressure from an aluminum reservoir tank. Its mass was measured with the precision balance and introduced into the measuring cell by means of a flexible high pressure capillary.

After preparation of a mixture of known composition and the desired temperature at low pressure was reached, the pressure was then slowly increased at constant temperature until the system becomes monophasic. The pressure at which the last bubble disappears represents the equilibrium pressure for the fixed temperature.

The purity of the IL is checked again by NMR at the end of the study to confirm that no degradation takes place during the measurements.

2.3. Thermodynamic modeling

As in previous works [11,12] we have applied the Peng–Robinson equation of state [32]:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b(V - b_m)} \quad (1)$$

where the constants a_m and b_m are expressed as functions of concentration of the different components in the mixture through the Wong–Sandler mixing rule [33]:

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \sum_i (x_i a_{ii} / b_{ii} RT) - (A_\infty^E / \Omega RT)} \quad (2)$$

$$a_m = b_m \left[\sum_i \frac{x_i a_{ii}}{b_{ii}} + \frac{A_\infty^E}{\Omega} \right] \quad (3)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{b_{ii} + b_{jj}}{2} - \frac{(1 - k_{ij}) \sqrt{a_{ii} a_{jj}}}{RT} \quad (4)$$

in these equations, a_m and b_m are the EoS constants, $\Omega = 0.34657$, and the excess Helmholtz free energy at the limit of infinite pressure, that is calculated assuming that $A_\infty^E \approx A_0^E \approx G_0^E$ where G_0^E is the excess Gibbs free energy at the limit of zero pressure calculated here using the UNIQUAC model [34].

The correlation of the experimental data was carried by the minimization of the objective function, OF , for

$$OF = \sum_{i=1}^N \left[\frac{p_{cal} - p_{exp}}{\sigma_p} \right]^2 \quad (5)$$

where N is the number of data points, P is the pressure, the superscripts “exp” and “cal” refers to the experimental and calculated values, respectively, and σ_p is the standard deviation of pressure. The experimental uncertainties in the pressure data were used for σ_p . The minimization method was performed using a genetic algorithm code, implemented and fully explained in Alvarez et al. [45]. The difference between experimental and calculated values was calculated as the average percent deviation, expressed in absolute form, as follows:

$$|\Delta P| = \frac{100}{N} \sum_{i=1}^N \left[\frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right] \quad (6)$$

Furthermore the proposed model was applied, in the diluted region limit, to determine the Henry’s constant for the studied systems.

3. Results and discussion

The solubility of carbon dioxide in the studied ILs was measured for mole fractions ranging from 0.2 to 0.8, in the temperature range 293–363 K and pressures from 0.6 to 74 MPa, as reported in Tables 1 and 2 and depicted in Fig. 1. A temperature increase leads to an increase on the equilibrium pressures and by increasing CO₂ concentration, the equilibrium pressures increase gradually, at first, and rapidly for higher CO₂ contents as also observed previously for other ILs [11,12].

The experimental data reported here is generally in agreement with those available in literature, covering however a wider range

of carbon dioxide concentrations, pressures and temperatures, as depicted in Fig. 2. For the system CO₂ + [C₄mim][Tf₂N] a good agreement is observed with the data by Shin et al. [46] for CO₂ mole fractions below 0.7. Above these concentrations, their data is scarce and ours provide a more detailed view of the phase diagram. The data by Anthony et al. [15] for this system is available only in the low pressure region and seems to present some deviations from both the data reported here and by Shin et al. [46]. For the system CO₂ + [C₄mim][DCA] only three isotherms below 10 MPa were reported by Aki et al. [13]. A good agreement is obtained with this data in the lower pressure region while again the data reported here provide a more complete description of the phase diagram for high pressures.

Contrary to what was expected, the higher basicity character of the dicyanamide anion, compared to the bis(trifluoromethylsulfonyl)imide, as expressed in their pK_a values, does not enhance the CO₂ solubility as was previously observed with the acetate anion. The explanation for this fact seems to be that, as shown previously [12], the solubility of CO₂ on an IL is enhanced by a Lewis acid/base interaction between the gas and the anion. The dicyanamide, in spite of its large pK_a value, seems however to be a much weaker Lewis base than the acetate anion.

3.1. Henry’s constants

The results of the application of the thermodynamic modeling to the binary systems containing ionic liquids studied in this work are presented in Table 3 for all the experimental data. In this table, T is the temperature, k_{12} , A_{12} and A_{21} are the interaction parameters of the model, where 1 stands for the CO₂ and 2 for the ionic liquid. This table is divided in sections for each system studied. The physical parameters used in the thermodynamic model are reported in Table 4 while the interaction parameters used are presented in Table 3. The proposed model, with temperature independent parameters, was applied to describe the experimental data and estimate the Henry’s constant for the studied systems. As depicted in Fig. 3 the model describes well the experimental data for pressures below 30 MPa. Above this pressure higher deviations are observed.

The Henry’s law relates the amount of a given gas dissolved in a given type and volume of liquid, at a constant temperature, to the fugacity of that gas in equilibrium with that liquid and can be described as

$$H_{12}(T, P) = \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \quad (7)$$

Table 1
Bubble point data of the system CO₂ (1) + [C₄mim][Tf₂N] (2).

x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa
0.231	292.65	0.629	0.319	293.21	0.915	0.404	293.53	1.410	0.503	293.22	1.997	0.602	293.27	3.052
0.231	303.18	0.786	0.319	303.05	1.223	0.404	303.10	1.812	0.503	303.12	2.568	0.602	303.31	3.962
0.231	313.32	1.050	0.319	313.19	1.540	0.404	313.17	2.273	0.503	313.10	3.196	0.602	313.13	4.912
0.231	323.22	1.303	0.319	323.27	1.892	0.404	323.26	2.787	0.503	323.20	3.909	0.602	323.13	6.015
0.231	333.19	1.574	0.319	333.17	2.283	0.404	333.23	3.316	0.503	333.12	4.670	0.602	333.20	7.269
0.231	343.00	1.874	0.319	342.87	2.682	0.404	343.11	3.897	0.503	343.24	5.499	0.602	343.02	8.675
0.231	353.20	2.179	0.319	353.09	3.121	0.404	353.12	4.512	0.503	353.17	6.412	0.602	353.20	10.196
0.231	363.26	2.485	0.319	363.19	3.579	0.404	363.17	5.156	0.503	363.18	7.372	0.602	363.23	11.776
x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa
0.701	293.37	4.433	0.749	293.32	5.907	0.771	293.42	12.829	0.801	293.26	33.263			
0.701	303.19	5.880	0.749	303.19	10.812	0.771	303.31	18.726	0.801	303.19	39.373			
0.701	313.11	7.860	0.749	313.12	15.810	0.771	313.23	23.943	0.801	313.25	44.740			
0.701	323.09	10.215	0.749	323.11	20.543	0.771	323.13	28.960	0.801	323.30	49.990			
0.701	333.10	13.150	0.749	333.17	25.124	0.771	333.28	33.693						
0.701	343.25	16.144	0.749	343.20	29.205	0.771	343.08	38.081						
0.701	353.14	19.437	0.749	353.09	33.219	0.771	353.22	42.030						
0.701	362.99	22.468	0.749	363.18	36.365	0.771	363.25	46.010						

Table 2
Bubble point data of the system CO₂ (1) + [C₄mim][DCA] (2).

x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa	x_1	T/K	P/MPa
0.200	293.36	1.018	0.300	293.50	1.980	0.410	293.38	3.015	0.507	293.44	4.496	0.601	293.41	32.606
0.200	303.45	1.360	0.300	303.40	2.590	0.410	303.45	3.950	0.507	302.91	6.056	0.601	303.14	39.866
0.200	313.36	1.771	0.300	313.06	3.230	0.410	313.32	5.088	0.507	313.03	8.856	0.601	313.17	46.749
0.200	322.94	2.260	0.300	323.04	4.005	0.410	323.47	6.395	0.507	322.93	13.184	0.601	323.07	53.174
0.200	332.72	2.644	0.300	333.28	4.860	0.410	333.13	7.743	0.507	333.21	17.566	0.601	333.15	59.007
0.200	343.12	3.108	0.300	343.34	5.776	0.410	343.01	9.452	0.507	343.12	21.750	0.601	343.17	64.217
0.200	353.09	3.745	0.300	353.10	6.722	0.410	353.13	11.166	0.507	353.01	25.759	0.601	353.19	69.002
0.200	363.25	4.328	0.300	363.11	7.776	0.410	363.18	13.106	0.507	363.20	29.583	0.601	363.21	73.640

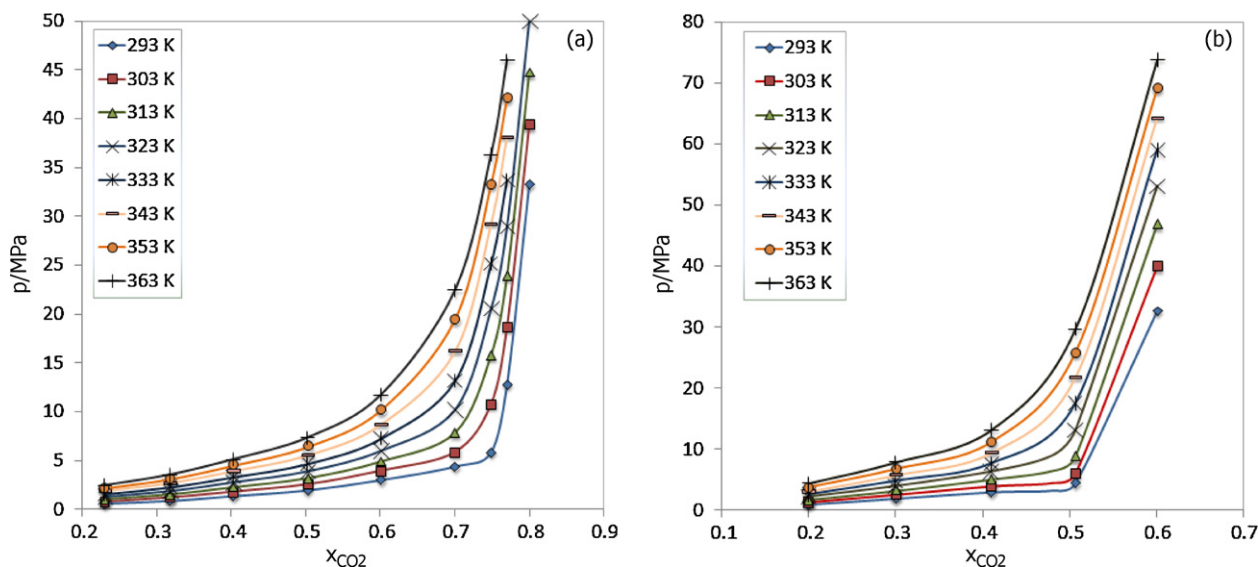


Fig. 1. Pressure–composition diagram of the binary systems (a) CO₂ + [C₄mim][Tf₂N] and (b) CO₂ + [C₄mim][DCA]. The solid curves are guide for easier visual interpretation.

where $H_{12}(T, P)$ is the Henry's constant, x_1 is the mole fraction of gas dissolved in the liquid phase, and f_1^L is the fugacity of the gas in the liquid phase. As shown, Eq. (7) is only rigorously valid in the diluted region limit. The Henry's constants for the CO₂ in the investigated ILs were estimated by fitting the PR-WS/UNIQUAC model to the data and calculating the limiting slope as the solubility approaches zero. This approach introduces some uncertainty on the estimated Henry's constants but the values of these constants for the two studied ILs are different enough to allow a discussion of the interactions between the CO₂ and the

two ionic liquids based on these values. The estimated Henry's constants results, reported in Table 3, indicate that Henry's constant increases slightly (i.e., CO₂ solubility decreases) with the temperature.

The results for the Henry's constant of CO₂ in [C₄mim][DCA] and in [C₄mim][Tf₂N] were correlated as a function of temperature by an empirical equation of the type:

$$\ln(H_{12}) = A \left(\frac{1}{T} \right) + B \quad (8)$$

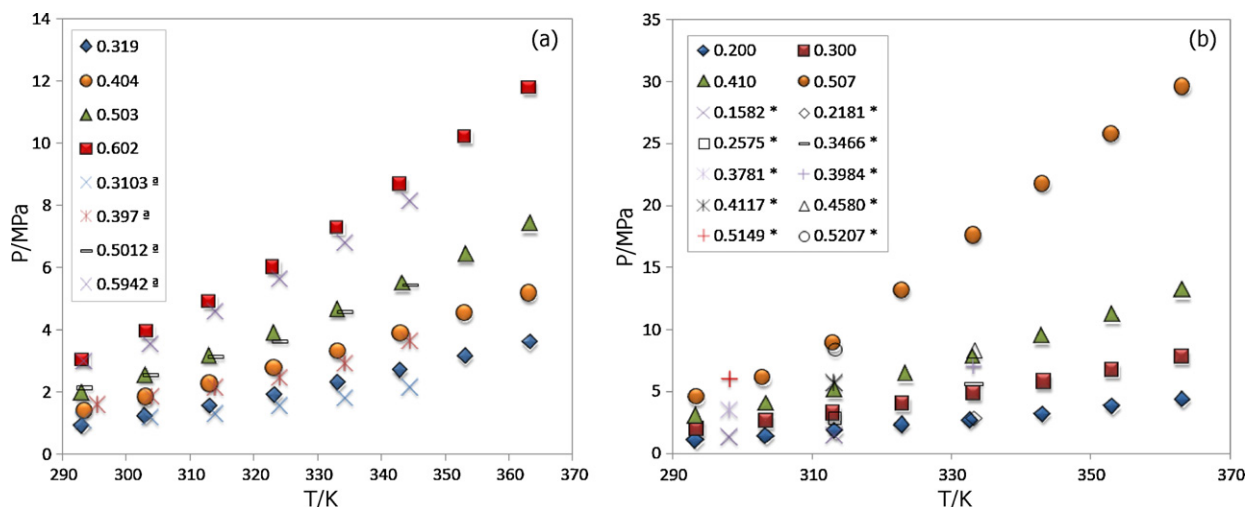


Fig. 2. Pressure–temperature–composition diagram of the binary systems (a) CO₂ + [C₄mim][Tf₂N] and (b) CO₂ + [C₄mim][DCA] for this work experimental data and data from ^aRefs. [46] and ^{*}Ref. [13].

Table 3
Interaction parameters for the studied systems and predicted Henry's constants.

CO ₂ + [C ₄ mim][DCA] ($K_{ij} = 0.1255, A_{12} = 5075.1963, A_{21} = -1168.4022, \Delta P = 5.2\%$)		CO ₂ + [C ₄ mim][Tf ₂ N] ($K_{ij} = 0.2734, A_{12} = 5888.6826, A_{21} = -1845.7030, \Delta P = 7.9\%$)	
T/K	H ₁₂ /MPa	T/K	H ₁₂ /MPa
294	5.13	294	2.05
298	5.59	298	2.25
303	6.19	303	2.53
313	7.49	313	3.14
323	8.92	323	3.84
333	10.48	333	4.62
343	12.14	343	5.47
348	13.01	348	5.93
353	13.90	353	6.41
363	15.74	363	7.42

Table 4
Properties of the substances used in the modeling.

Compound	T _c /K	P _c /MPa	ω	r	q
CO ₂	304.21 ^a	7.38 ^a	0.2236 ^a	3.26 ^c	2.38 ^c
[C ₄ mim][DCA]	782.96 ^b	2.44 ^b	0.8419 ^b	22.63 ^c	14.86 ^c
[C ₄ mim][Tf ₂ N]	826.30 ^b	2.76 ^b	0.3004 ^b	32.67 ^c	20.68 ^c

^a Ref. [48].

^b Calculated with Ref. [49].

^c Calculated with Ref. [50].

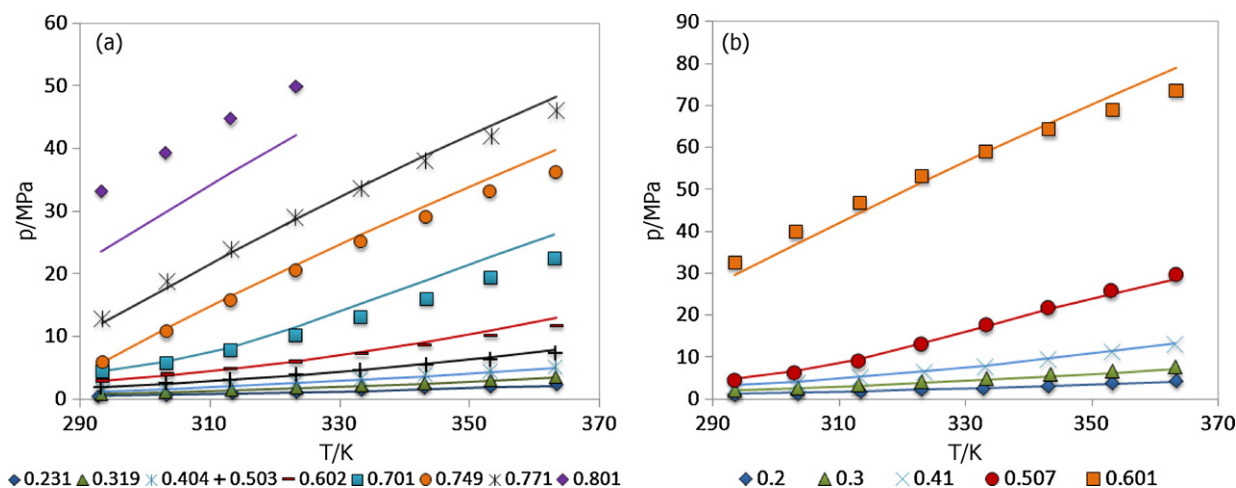


Fig. 3. PTx diagram and modeling for the systems CO₂ + [C₄mim][Tf₂N] (a) and CO₂ + [C₄mim][DCA] (b). The solid lines represent the calculations with PR-WS/NRTL EoS.

where the coefficients A and B are listed in Table 5, together with the Henry's constant average absolute deviations, $|\Delta H_{12}|$, obtained for each ionic liquid.

The effect of temperature on CO₂ solubility can be related to the Gibbs energy, the partial molar entropy and partial molar enthalpy of solvation [47] and can be calculated from an appropriate correlation of Henry's constant:

$$\Delta_{\text{solv}}G^\circ = RT(\ln(H_{12}))_p \quad (9)$$

$$\Delta_{\text{solv}}H^\circ = -T^2 \left(\frac{\partial \Delta_{\text{solv}}G^\circ}{\partial T} \right)_T = -RT^2 \left(\frac{\partial \ln H_{12}}{\partial T} \right)_p = RA \quad (10)$$

$$\begin{aligned} \Delta_{\text{solv}}S^\circ &= \frac{\Delta_{\text{solv}}H^\circ - \Delta_{\text{solv}}G^\circ}{T} = -RT \left(\frac{\partial \ln H_{12}}{\partial T} \right)_p - R \ln(H_{12})_p \\ &= -RB \end{aligned} \quad (11)$$

The partial molar enthalpy of solvation gives an indication of the strength of interactions between the gas and the IL, while the partial molar entropy illustrates the amount of ordering present in the gas/IL mixture. The results presented in Table 5 show that the partial entropies in both fluids are essentially identical, indicating a similar structural solvation interaction. The partial molar enthalpy of solvation of the CO₂ in [C₄mim][Tf₂N] is lower than in [C₄mim][DCA], indicating a slightly stronger interaction between the CO₂ and

Table 5
Coefficients A and B in Eq. (8) and partial molar enthalpy and partial molar entropy of solvation obtained for CO₂ (1) + ILs (2) systems.

Ionic liquid	A	B	$ \Delta H_{12} /\%$	$\Delta_{\text{solv}}H/\text{kJ mol}^{-1}$	$\Delta_{\text{solv}}S/\text{J mol}^{-1} \text{K}^{-1}$	$-T \Delta_{\text{solv}}S _{T=298 \text{ K}}/\text{kJ mol}^{-1}$
[C ₄ mim][DCA]	-1739.868	7.564	0.71	-15.03	-64.75	19.29
[C ₄ mim][Tf ₂ N]	-1970.775	7.456	0.60	-18.21	-68.09	20.29

the [C₄mim][Tf₂N] when compared with the [C₄mim][DCA]. The enthalpies and entropies of solvation contribution make the solubility of both systems non-spontaneous and moreover, controlled by physical absorption. The partial molar enthalpies of solvation observed for these ILs are also much lower than those previously reported for [C₄mim][acetate] and [C₄mim][TFA] [12] showing that, as discussed previously, in spite of the pK_a of dicyanamide no acid/base interaction is observed for the ILs studied in this work.

4. Conclusions

New gas–liquid equilibrium data of two binary systems, namely, 1-butyl-3-methylimidazolium dicyanamide + CO₂ and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + CO₂ have been investigated in a wide range of temperatures, pressures and CO₂ mole fractions aiming at understanding the effect of the basicity of the anion in the gas solubility in the ionic liquids.

Contrary to what the dicyanamide anion basicity would suggest the [C₄mim][DCA] ionic liquid do not show a significant enhancement on the CO₂ solubility. In fact, the interaction between the negative fluorine atoms and the positive charge on the carbon of the CO₂ molecule seems to be stronger in the Tf₂N anion based IL.

A thermodynamic model based on the Peng–Robinson EoS with the Wong–Sandler/UNIQUAC mixing rule was used in description of the measured data. The model allows a good description of the experimental data and the estimation of the Henry's constants for these systems.

The partial Gibbs energy, enthalpies and entropies of solvation estimated from Henry's constants show that the solubility of CO₂ in both systems is non spontaneous at standard pressure (0.1 MPa). The entropies of solvation in the two systems are essentially identical and the partial molar enthalpy of solvation of CO₂ in [C₄mim][Tf₂N], when compared to the one of [C₄mim][DCA], indicate similar interactions between the CO₂ and the two ionic liquids.

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